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EXPERIMENTAL STUDIES ON BREDIG GOLD HYDROSOLS

DISSERTATION

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JAMES HEYWARD YOUNG

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I. Introduction.

Aqueous solutions of colloidal gold have been the object of extensive investigations since the time of Faraday[1]. In particular, the method for making these solutions discovered by Bredig[2, 3] in 1898 has attracted much attention on account of its seeming simplicity. Unfortunately, the very simplicity attendant upon striking an arc between gold wires under water served for a long time to obscure the nature of the colloid.

It is now generally believed that many or even most hydrophobic colloids are complex units in which an insoluble material is associated or combined with a smaller quantity of a water-soluble component[4, 5, 6, 7]. It is further believed that true solution forces acting upon this water-soluble component serve to a considerable extent in accounting for the stability and other properties of the colloids[8, 9]. One still sees statements, however, that the noble metal sols and particularly Bredig's gold sols are substantially gold finely dispersed in water[10, 11].

This difference in opinion as to the nature of Bredig's colloidal gold has been, and to some extent still is, due to work done in improperly defined systems where so many sources of error exist that important factors are left out of consideration.

The scope, limitations and difficulties attendant upon the problem will, it is believed, be most readily appreciated if prior investigations are briefly reviewed in the light of the variables or sources of error recognized and investigated. For convenience these may be grouped in the following experimental categories:

1. The system before synthesis.

2. The system during synthesis.
3. Measurements.

The System before Synthesis.

Faraday[1] was apparently the first to emphasize cleanliness.

Bredig[12] noted that his colloidal gold was most readily made if a small amount of alkali was present in the water. He did not deem such additions essential however.

Beans and Eastlack[13] in 1915 were the first to investigate and prove experimentally that electrolyte was a necessary factor for colloid formation. This source of error previous to their investigation had led most chemists to believe that a Bredig gold sol resulted solely from dispersing gold in a sufficiently fine form in water. Beans and Eastlack showed that not only was an electrolyte necessary but a particular electrolyte of the type which furnishes an anion with which gold ordinarily forms chemical compounds was required. Water of measured purity, purified gold, resistance glassware, purified electrolytes, careful exclusion of outside contamination and a sensitive method of measurement further enabled these investigators to fix the amount of electrolyte as about 0.1 M to 0.00001 M, upper and lower limits repectively. It is most unfortunate that the careful definition of the presynthesis system made by Beans and Eastlack has not received the attention it deserves in many places, because changes in the system during synthesis are difficult to interpret without these precautions.

The System during Synthesis

Svedberg[14, 15, 16, 17] has thoroughly studied the effect of varied electrical circuits on the size of the colloidal particles formed and the decomposing effect of the current on certain organic media. An oscillatory discharge, small capacity, low self-induction, and a small spark gap produce smaller particles. The same conditions except for an increase in capacity favor less decomposition of the medium.

Amsden[18] showed that a D. C. arc in water-potassium chloride causes electrolysis. He further showed that no appreciable electrolysis results with a modified oscillatory arc.

The effect of changes in temperature and stirring during synthesis have not been thoroughly investigated. Bredig[12], Svedberg[10] and Beans and coworkers[20, 21, 22] recommend cooling. Stirring is also recommended.

During the synthesis particles of various sizes are formed. These may be roughly classed as sludge and colloidal. Svedberg with Borjeson[23], Rinde[24] and others showed that a distinct gap in size separates the coarse sludge from the colloid. The colloid does not seem uniform in size, however, so that at best an estimation of size represents an average. Beans with Beaver[25] took steps to eliminate the non-colloidal material which is formed in arcing gold beneath water. They arbitrarily drew a dividing line by subjecting the colloidal solutions before measurements were made to the action of centrifugal force approximately equal to 1200 times gravity. Low's[26] work indicates that centrifuging a sol dilute in gold made in 0.001 M potassium chloride-water at 1200 times gravity for one hour probably removes all coarse particles or sludge and leaves a sol of fairly reproducible particle size.

These results are also apparent in the work of Beans with Briggs[20], Davidson[22] and others. Furthermore, these investigators were able to show that different electrolytes, varying electrolyte concentrations and continued arcing cause changes in the stability of the particle. For sols made in potassium chloride-water, the optimum amount of potassium chloride is apparently between 0.001 M and 0.002 M. From the observations of Low and Amsden that the sols are unstable during the first short arcing period and the work of Rugar[27] showing that the sols contain a larger ratio of stable colloid when the gold-chloride ratio lies between certain limits, it appears that the optimum conditions for the existence of Bredig's sol in alkali and alkali metal chloride aqueous solutions is contingent on the ratio concentration of colloid: concentration of electrolyte in its aqueous dispersion medium.

Discussion of Previous Measurements.

Many measurements have been made on Bredig's colloidal gold. Space permits only a brief review here. We will restrict ourselves to those investigations in which conditions before and during synthesis most closely approach the optimal and in particular to those which bear directly on the present problem. Since methods of measurement in this field fall short of the desired quantitative precision, no rigid comparisons are possible.

To summarize briefly, prior investigators have demonstrated within a reasonable certainty that measurements on Bredig gold sols in aqueous media are most likely to be reproducible and comparable if before synthesis the following conditions exist:

1. The water should be of measured purity, preferably of specific conductivity below 1.3×10^{-6} mhos.
2. Purified electrolyte giving an anion with which gold forms compounds, in a quantity within the range of 0.01 M to 0.0001 M should be present. For alkali chlorides the optimum range is apparently between 0.001 M and 0.002 M.
3. Outside contamination must be rigidly excluded and resistance glassware employed.

During synthesis the following conditions are preferable:

1. An oscillating arc.
2. A small arc gap.
3. Vigorous stirring.
4. Cooling below 20° C.
5. Some capacity.

Since Beans and Eastlack[13] showed that a certain kind and amount of electrolyte was necessary for stable Bredig sols in water, several attempts have been made to determine what role the electrolyte plays in the formation of the colloid.

Beaver[25] produced an arc with D. C. in water of initial specific conductivity around 1.2×10^{-6} mhos to which potassium chloride, hydrogen chloride or sodium hydroxide in a concentration of about 0.001 M had been added. After arcing had dispersed about 500 mg. of gold per liter in his water-electrolyte medium, he titrated the sols with sodium hydroxide or silver nitrate, using conductivity to determine the end-point of the titration and the reactive electrolyte present. From a comparison of titrated sols with titrated electrolyte-water portions which had not been arced, he concluded that part of the anions are removed during the colloid formation while the cations, to the contrary, remain reactive in the medium. The amount of anion removed appeared roughly proportional to the gold present as colloid.

Shear[28] with a D. C. arc and Amsden[18] with an oscillatory arc dispersed varying amounts of gold within aqueous potassium chloride solutions where the potassium chloride concentration ranged from a few ten thousandths molar to several thousandths molar. Layton[29] employed similar media but removed his arc from contact with the medium. A cell of the type

$$\text{Ag—AgCl—0.005 M KCl : : Sol—AgCl—Ag}$$

was then employed to measure the activities of the chloride ions in the sols. These investigators found that the activity of the negative ions always decreases coincidentally with colloid formation.

Although the evidence of the investigators clearly indicates that the Bredig sols formed by dispersing gold in water-electrolyte media are complex and that the colloid is probably composed of gold associated with negative ions of the type with which gold ordinarily forms compounds, the following brief analysis shows that the role played by the electrolyte has not been adequately established:

1. The results of various investigators are not in agreement as regards the following experimental relationships:
    (a) The ratio of gold to electrolyte in the colloid.
    (b) The effect of centrifugal force at 1200 times gravity on the electrolyte distribution.

(c) The effect of freezing on disrupting the particle.

2. The arcing device was unsatisfactory.

3. No measurements have been made on a system where it was experimentally shown that no equilibrium disturbing electrolyte was introduced before synthesis, during synthesis or during measurement.

4. The effect of the coarse material or sludge which has always been obtained, on changes in the electrolyte during the colloid formation was unknown.

5. Conductimetric titrations of sols containing any considerable amount of gold cause precipitation of the colloid. It cannot be taken as an assured fact that the addition of other electrolytes to the system does not alter the equilibrium.

6. Potentiometric measurements involve large errors of measurement in dilute sols, and in concentrated sols the electrodes do not function properly.

7. No measurements on sols containing less than 200 mg. of gold per liter have been made.

8. No measurements have shown that stable values which did not change appreciably with time were obtained.

II. The Object of This Investigation.

This investigation was undertaken for the following reasons:

1. To minimize or remove some of the uncertainties accompanying previous investigations.

2. To accumulate additional data on the redistribution of electrolyte which accompanies the formation of Bredig aqueous gold sols by using a different method of measurement.

3. With the hope that these measurements might serve to increase the knowledge of the nature of this colloid.

III. Measurements.

The measurements of this investigation fall logically into three divisions:

1. Experimental checks were employed to eliminate variables from the system before and during synthesis.

2. Changes in the electrolyte distribution after sol formation were followed by conductivity measurements.

3. Since it became apparent that the values for the electrolyte-gold relationship found in (2) in part agreed and were in part at variance with the results of preceding investigations, some conductimetric titrations by Beaver's method and some activity measurements after the method of Shear, Amsden and Layton were made.

Part 1. Checks on the System.

A. The System before Synthesis.

The Water.

Ordinary distilled water having a specific conductivity of about 1.3 x 10^{-6} mhos was redistilled from Pyrex glass through a block tin condenser. The middle portion was collected in non-sol glass bottles in the presence of live steam. The water was measured directly before using in a conductivity cell of the type described by Beans and Eastlack[13], and that employed ranged in specific conductivity between 1.0 and 1.2 x 10^{-6} mhos.

The electrolyte.

J. T. Baker's C. P. potassium chloride was recrystallized twice from this conductivity water. The salt was then dried in platinum, ground in an agate mortar, and kept in a glass stoppered bottle in a desiccator. Solutions were made by diluting the requisite amount of precisely weighed salt with conductivity water in calibrated one liter volumetric flasks.

The gold.

The gold wire employed was obtained through Baker and Co., who made the same from "mint gold" analyzing

99.99% gold. The gold when tested spectroscopically showed traces of manganese and iron. Sensitive qualitative tests on a solution from a gram sample gave no evidence of the presence of these impurities. Negligible amounts are apparently present. The gold was fused at right angles to platinum wire by hanging small gold wire angles on the end of the platinum wire and heating with a blast lamp. Before used the gold was cleaned in concentrated nitric acid, concentrated hydrochloric acid, alternately heated to redness and washed in conductivity water several times. finally cooled and rinsed with the solution to be arced.

Glassware.

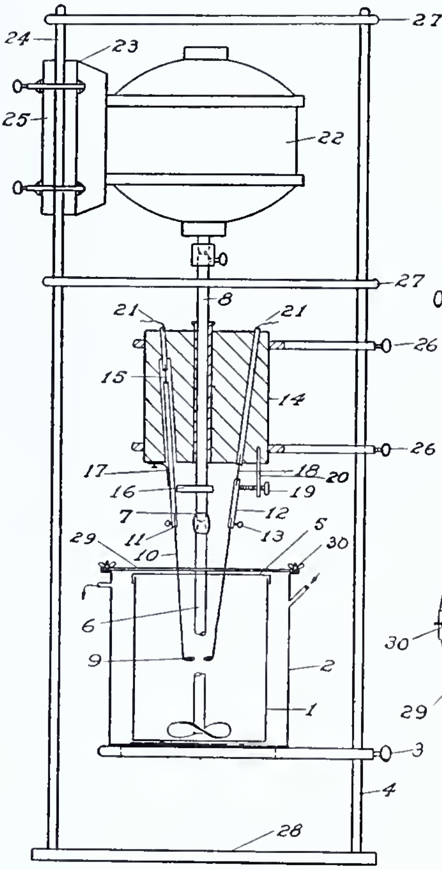
Pyrex or non-sol glass was employed whenever the solution remained in contact with said glass for more than a few minutes. The solutions except during transfer from one vessel to another remained in closed vessels. The glass was cleaned, steamed and finally rinsed with several portions of the solution to be handled or measured therein.

B. The System during Synthesis.

The Arcing Device.

The arcing device developed here provides for stirring, cooling and semi-automatic arcing in one adjustable, compact mechanism which experiment has shown to be substantially free from contamination during the synthesis. Referring to the accompanying drawing, Fig. I shows the apparatus in elevation. The potassium chloride solution is placed in beaker 1, which rests within the water jacket 2, which is adjustably attached by ring 3 to the upright rod 4. The beaker is capped with the flanged glass cover 5. The glass stirrer 6 extends from the solution through a hole in the cover to the chuck 7 on the end of the drive shaft 8. Pieces of gold 9 form the arcing surface. These are fused at right angles to platinum wires 10 which extend from the solution through the cover to drilled brass rods 11 and 12 into which the wires are inserted and held in place by set screws 13. The brass rods are imbedded and insulated from one another in the hard rubber cylinder 14. The middle of rod 11 contains the steel spring 15 and the cylinder 14 is hollowed out from the spring downward which permits the lower part of 11 to move outward when actuated by the fibrous eccentric 16 which is attached to drive shaft 8. A spring 17 presses rod 11 back into place as the ec-

FIG. I
ARCING APPARATUS



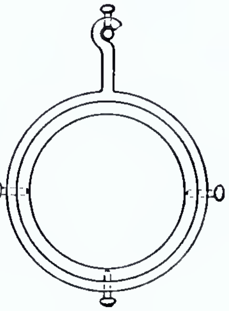


FIG. I-A

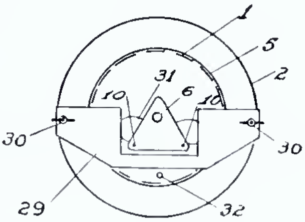


FIG I-B

centric pressure is released. The gold at the solution terminus of 11 thus moves into contact with and away from the gold at the end of 12 with each revolution of the drive shaft 8. Rod 12 also contains a flat spring junction at 18. A set screw 19, through the brass rod 20, embedded in the rubber cylinder 14, acts against the lower part of rod 12 and the gold terminating 12 should be laterally adjusted to contact with the gold terminating 11 when the eccentric is exerting a minimum push on 11. The upper ends of rods 11 and 12 are soldered to clips 21 through which the electrical connection is made.

Drive shaft 8 is attached to motor 22 which in turn is bolted to a brass plate 23 grooved to fit against upright rods 24 and bolted to a smaller brass plate 25 on the opposite side of rods 24. This permits vertical adjustment of the motor at will.

The rubber cylinder 14 is attached by iron rings 26 to upright rod 4. The rings are larger than the cylinder and are pierced by three set screws acting around the periphery of cylinder 14, as shown in Fig. I A. A vertical and horizontal adjustment of cylinder 14 is thus possible. Water jacket 2 is similarly adjustable. The rods 24 and 4 are cross braced at 27 and the iron base 28 securely bolted down to reduce vibration.

Fig. I B shows the beaker 1, glass cover 5, and water jacket 2 in plan. The glass cover and beaker are held firmly within the water jacket by the aluminum piece 29 clamped to the water jacket by bolts and lugs 30. To further protect the solution in 1 from contamination, a cloth 31 is clamped on top of glass cover 5 and under aluminum piece 29 so as to completely cover the hole where stirrer 6 and wires 10 enter the solution. The glass cover is provided with a hole 32 fitted with a removable glass stopper. A thermometer may be inserted or the solution may be withdrawn through this hole without disturbing the set up.

The above apparatus is not entirely satisfactory but it does possess certain advantages over the type formerly used. The more important improvements are:

1. Continuous arcing can be produced which has lasted under some conditions for thirty minutes without adjustment of the arcing surfaces. Readjustment is easily made.

2. The solution is more completely protected from outside contamination.

3. An arc can be obtained with more widely varied electrical conditions than previous investigators have found possible.

4. The formation of coarse residue concomitant with the formation of the colloid can be almost entirely avoided. Not only can the amount formed be considerably diminished, but that obtained resembles finely divided gold rather than the "sludge" described by Low[26]. Since the same apparatus can also be made to produce sols with "sludge" it has been possible to compare sols and thus evaluate electrolyte removal by the "sludge", thereby substituting experimetal data in the place of uncertainty.

5. The medium to be arced is now jacketed in such a way that the cooling can be done by running water, brine, or if necessary, a cooling medium pumped from a thermostat without danger of outside contamination.

The arcing device was given a number of preliminary tests to determine its suitability and flexibility.

Tests on Contamination.

Potassium chloride solutions were made and their resistance measured in Freas conductivity cells. Portions of the same potassium chloride solutions were then placed in the arcing device without current flowing but with other conditions the same as during arcing. Portions of the solutions were removed and measured in the Freas cells from time to time. The data in the following table shows that solutions may be transferred to and employed in this apparatus without measurable contamination from outside sources.

TABLE 1.

Measurements on Contamination

	Resistance in ohms at 25° C. ± 0.002	
	Cell 70	Cell 71
KCl (approx. 0.001 M)	2366	2367
	2365	2367
After 15 minutes operation	2366	2367
	2366	2367
" 30 " "	2366	2365
	2365	2367
" 60 " "	2366	2367
KCl 0.001 M	2375	2377
	2375	2377
After 1 hour operation	2375	2377
" 2 " "	2375	2377
" 3 " "	2376	2377

Tests for Electrolysis.

Potassium chloride solutions were placed in the arcing apparatus and the arcing surfaces spread far enough apart to give no arc. The current was turned on. The electrical circuit consisted of 110 volts A. C. with 16 ohms in series with the arc gap and a 1 M. F. condenser in parallel. At varying times portions of the solution were removed to conductivity cells for comparison with the original potassium chloride solution. Characteristic data follows.

TABLE 2.

Measurements on Electrolysis

	Resistance in ohms at 25° C. ± 0.002	
	Cell 70	Cell 71
KCl — original 0.001 M	2374	2376
Operated 30 minutes	2375	2376
" 60 "	2375	2378
" 90 "	2375	2378
" 120 "	2375	
Stood 1 day	2375	
KCl — original 0.001 M	2375	2376
Operated 45 minutes	2375	2376
" 75 "	2374	2376

Various sols were also tested with potassium iodide and starch, after precipitating the gold, in the manner described by Amsden[18]. No blue color developed. It may be noted that the potassium iodide if not freed of potassium iodate will give a light brown stain on reaction of the potassium iodate with the acid present after precipitation. Sols tested with alkaline hydrogen peroxide showed no traces of ionic gold.

From the above experimental proof it may be assumed that there is no appreciable electrolysis during the formation of the sols herein described.

Preliminary Sols.

The apparatus was further tested by making, or attempting to make, a number of preliminary sols therein. Table 3 below shows by comparing groups 1 and 2, that the apparatus functions over a wide range of electrical conditions and will give, if properly operated, substantially sludge-free sols. Group 1 also serves to extend somewhat the postulate of Beans and Eastlack that only those anions which form compounds with gold serve as stabilizers and only in definite concentrations. Finally the discovery made by the author and investigated by Low, that a colloid results if gold is arced in conductivity water and electrolyte added after the arc is discontinued, is extended to include hydrogen chloride and sodium hydroxide in a system where outside contamination has been experimentally shown to be negligible. This is shown in group 3.

TABLE 3.

Preliminary Sols

Group 1

No.	Medium	Electrical Circuit	Color Sol	Color Residue	Remarks
1.	H_2O sp. c. $1x10^{-6}$	110v. 40 ohms. A.C. 1M.F.	black	black	ppct. within 12 hr.
2.	KCl 0.001 M	same	red	dark	stood in non-sol bottle 2 years—small gold ppt. on bottom bottle
3.	KCl 0.001 M	same	red	brown	stable
4.	KCl 0.005 M	same	red	brown	stable
5.	KCl 0.01 M	same	dark	dark	unstable suspension settles slowly; ppct. completely by centrifuging 15 min. 1200 x gravity
6.	K_2CrO_4 0.001 M	same	black	dark	suspension settles within 12 hr.
7.	$KMnO_4$ 0.001 M	same	black	dark	suspension settles within 12 hr.
8.	NaCl 0.001 M	same	red	brown	stable
9.	HCl 0.001 M	same	rose-red	brown	stable
10.	NaOH 0.001 M	same	red	brown	stable

Group 2

No.	Medium	Electrical Circuit	Color Sol	Color Residue	Remarks
11.	KCl 0.001 M	110 v. 15 o. A.C. no cap.	red	none	stable
12.	KCl 0.001 M	110 v. 40 o. A.C. no cap.	red	none	stable
13.	KCl 0.001 M	16 v. 10 o. A.C. no cap.	red	none	stable
14.	KCl 0.001 M	10 v. 15 o. A.C. no cap.	red	none	stable
15.	KCl 0.001 M	6 v. 20 o. A.C. no cap	red	none	stable

A small yellow residue of gold settled out of these sols on standing.

Group 3

The sols were made by striking an arc for 15 minutes under 250 cc. of water of specific conductivity 1.1-1.2 x 10^{-6} mhos. After removing 50 cc. of the unstabilized mix for comparison, 50 cc. of electrolyte solution were added to give the approximate concentrations noted in the table and the mixture stirred without further arcing.

No.	Electrolyte	Stirred	Appearance Before Adding Electrolyte	Appearance After Adding Electrolyte and Stirring	Stability
16.	HCl 0.001 M	30 min.	black	rose red	not ppct. by centrifuging 15 min. 1200 x g.
16a.	Unstabilized mix	none	black		ppct. on centrifuging
17.	NaOH 0.001 M	30 min.	black	wine red	not ppct. by centrifuging
17a.	Unstabilized mix	none	black		ppct. on standing in non-sol bottle over night
18.	NaCl 0.001 M	30 min.	black	red	stable to centrifuging 30 min. 1200 x g.
18a.	Unstabilized mix	60 min.	black		ppct. by stirring

Part 2.

Measurements on the Electrolyte-Gold Relationship.

Discussion of the Method of Measurement Employed.

The necessary preliminary modifications and investigations of the arcing device and variables before and during synthesis having been made, a method of measuring the change in the electrolyte distribution and its relationship to the gold present as colloid was next considered.

Conductivity cells of the Freas type having electrodes of bare platinum were selected upon the following considerations:

1. Sols may be measured therein without introducing impurities.

2. Such cells are sensitive to small electrolyte changes.

3. It had been experimentally shown that the 0.001 M potassium chloride-water solutions here employed could be transferred and arced without contamination.

4. Amsden[18], Low[26] and the author found no measurable electrolysis with the oscillating type of arc here employed.

5. Nordlund[30] and Svedberg and Pope[31] respectively had observed that mercury and cadmium sols in alcohol showed a decrease in conductivity as compared with the media before sol formation. Beaver made the same observation with gold sols in potassium chloride and hydrogen chloride.

6. Beaver, Amsden, Shear and Layton showed that chloride ions are removed during colloid formation.

7. Bjerrum[32] with chromium sols, Pennycuick[33, 34, 35] with platinum sols, Pauli[36] and Beaver[25] with gold sols have advanced evidence indicating that electrolyte other than that taking part in the colloid formation is present in a substantially measurable condition.

8. Zsigmondy[37], Freundlich[38], Svedberg[39], von Hevesy[40], Nordenson[41], Beans and Eastlack[13], and Pennycuick[33] considered the conductivity of the colloid itself very small. No reliable measurements have been made, but values varying from a specific conductivity of about 1.2×10^{-7} mhos to 2×10^{-11} mhos have been assigned to particles of the size believed to preponderate in Bredig sols of the type with which this investigation is concerned.

Apparatus.

All measurements were made in a water thermostat equipped with a Beaver[42] regulator, at 25°C ± 0.002. The Beckmann thermometer was checked against one certified by the U. S. Bureau of Standards.

The conductivity set-up consisted of a vacuum tube oscillator operating at 1000 cycles which was tuned and checked against a Vreeland oscillator at the same frequency. A two stage audio-amplifier was used to assist the precise location of the point of balance. The Kohlrausch slide wire used corresponds to the one designated as No. 4258 by Leeds and Northrup in their catalogue No. 48 (1927). One two dial Curtis coil box, Leeds and Northrup No. 4656, and one three dial bifilar wound coil box, Leeds and Northrup No. 4711w, were employed in the resistance arm of the circuit. Three variable, rotary, air condensers giving up to 0.003 m. f. were used to balance capacity in the cell.

Preliminary Measurements.

A number of preliminary sols were made to determine whether any change in electrolyte distribution occurred coincident with sol formation. Potassium chloride solutions were introduced into the arcing apparatus, stirred for a few minutes, the resistance measured, and then arced for varying periods. Characteristic data given in Table 4 shows that the electrolyte concentration apparently decreases steadily as arcing continues. The sols gave no indication of chlorine or gold ions when tested as previously described. No determination was made on the gold content.

TABLE 4.

No.	Electrolyte	Cell	Volume Arced	Time of Arcing	Resistance Before Arcing	Resistance After Arcing
19.	KCl 0.001 M	70	200 cc.	15 min.	2377 ohms	2384 ohms
20.	KCl 0.001 M	70	200 cc.	30 "	2377 "	2391 "
21.	KCl 0.001 M	70	200 cc.	45 "	2377 "	2399 "
22.	KCl 0.001 M	70	200 cc.	60 "	2374 "	2414 "
23.	KCl 0.001 M	71	200 cc.	90 "	2376 "	2434 "

Calibration of Cells.

In order to determine how much electrolyte was being removed and whether the same bore any relationship to the colloid formed, two cells were calibrated by introducing therein carefully diluted samples of potassium chloride made from precisely weighed samples. No precision beyond the nearest ohm was attempted inasmuch as various measurements on the same sols had been found to vary by 2 ohms. Calibration data follows.

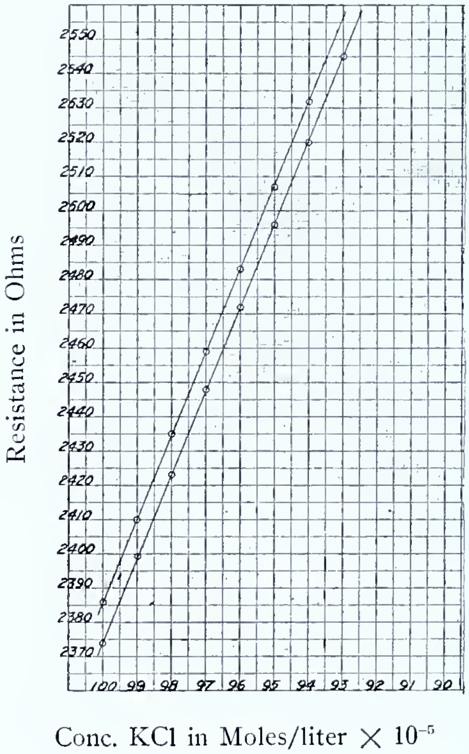


FIG. 1

Calibration of Freas Conductivity Cells with Bare Platinum Electrodes Against KCl Solutions

T= 25 ± 0.002°C

TABLE 5.

Calibration of Cells

Conc. of KCl	R Cell 70	R Cell 71
0.00100 M	2374	2377
	2375	2376
	2374	
0.00099 M	2400	2400
	2399	2401
0.00098 M	2424	2425
	2423	2424
0.00097 M	2448	2449
	2448	2450
0.00096 M	2472	2474
	2471	2473
0.00095 M	2495	2498
	2496	2497
0.00094 M	2520	2522
	2520	2522
0.00093 M	2544	2546
	2545	2546

From this data the curve shown in Fig. 1 was drawn and from the curve the electrolyte concentration in the sols was estimated.

Effect of Centrifuging on the Gold Content.

An attempt was next made to compare the electrolyte changes with the amount of the colloid formed by the following electrolyte changes with the calibrated conductivity cells, and the colloid formed by precipitating and weighing the gold from a measured portion of the sol. Practically all determinations were made in duplicate. The sols were precipitated with hydrochloric acid, filtered in porous bottom porcelain crucibles and the crucibles weighed after heating on a silica plate and cooling in a desiccator.

The sols were made, transferred to non-sol bottles and placed in a thermostat for one week. The conductivities and gold content were determined. Portions of five of these sols were then centrifuged for one hour at 1200 x gravity and the gold content redetermined. It is apparent from the data given in Table 6 that there is no definite relationship between the gold and the electrolyte change in those sols which have not been centrifuged. On the contrary, the centrifuged sols appear to show that a definite relationship does exist. All sols thereafter were centrifuged before measuring the gold content.

TABLE 6.

	Arcing	KCl Loss	Gold in Sol-At. Wts./L		Ratio Au : KCl	
Sol	Time	Moles/Liter	Uncentrifuged	Centrifuged	Uncentr.	Centr.
52.	15 min.	1.25×10^{-5}	6.95×10^{-4}	5.48×10^{-4}	56 : 1	44 : 1
39.	30 “	1.41	10.2	6.40	72 : 1	45 : 1
69.	45 “	1.25	8.77		70 : 1	
26.	30 “	1.29	15.4	5.64	119 : 1	44 : 1
27.	60 “	2.16	20.4	7.46	95 : 1	35 : 1
35.	90 “	2.56	15.6	11.6	61 : 1	45 : 1

Effect of Centrifuging on Electrolyte Distribution.

Portions of the sols after centrifuging at 1200 x gravity for one hour were placed in conductivity cells to determine whether any changes in the electrolyte distribution occurred during this centrifuging. No changes were found. Data follow.

TABLE 7.

Comparison of Conductivity of Sols Before
and After Centrifuging

One Hour at About 1200 x Gravity

Sol	Before Centrifuging		After Centrifuging	
	Cell 70	Cell 71	Cell 70	Cell 71
24.	2404		2406	
25.	2440	2442	2440	2441
26.	2441	2442	2442	2440
27.	2406	2407	2406	2407
28.	2427	2428	2427	2428
29.	2437		2437	

Electrolyte in the Sludge.

Svedberg, Low, Amsden and others have noted that the Bredig arc ordinarily produces not only colloidal material but also a coarse, non-colloidal precipitate which has been called "sludge". If this sludge removes electrolyte by adsorption or occlusion, then measurements on the electrolyte apparently removed as part of the colloid are subject to an unknown error. In the present investigation an attempt was made to evaluate the effect of the sludge in removing electrolyte by two methods.

The first method consisted in comparing sols in which no appreciable sludge was formed with those in which sludge formation was similar in extent and character to that described by Amsden and Low.

By the second method the sludge was removed and actually tested for the presence of electrolyte. In this case the sludge was transferred to a Monroe[43] crucible by washing it into the crucible with a small amount of the sol from which it was made. An inverted oversized Gooch funnel was placed over the crucible and made air-tight with a rubber cushion placed on the outside of the funnel in which the crucible rested. This cover funnel was connected by rubber tubing to a tube packed with cotton. The air sucked through the crucible was thus first filtered. Suction was applied and the sludge sucked dry. The crucible was then removed and placed on a silica triangle which in turn rested on a silica plate. The bottom of the crucible was held just above the plate. The cover was placed on the crucible which was then heated. During the heating the character of the sludge undergoes a very considerable change. The brown or black finely divided metal disappears, it bulk decreases greatly and a mat of yellow gold is formed. This change, it is believed, would of necessity free a part or all of any occluded, adsorbed or even combined electrolyte. Since the top of the crucible was covered and cooled somewhat, any volatilized electrolyte should condense therein. The crucible was next cooled and transferred to the suction jar. A clean conductivity cell was introduced beneath the funnel to catch liquid from the crucible. The cover was removed and carefully rinsed into the crucible with about 10 cc. of 0.001 M or 0.002 M potassium chloride. Two other 10 cc. potassium chloride portions were then employed to rinse down the sides of the crucible. After the filter train had been connected, the crucible was sucked dry. The conductivity of the potassium chloride solution was then measured in the cell in which it had been collected.

Preliminary experiments in which potassium chloride of the above concentrations were run through the Monroe crucible as above but without sludge present, indicated that all the potassium chloride solution could not be removed by suction, and in consequence a greater conductivity always resulted when the potassium chloride was collected after the crucible had been heated. These blanks were reproducible however. A second series of blanks was run with sludge in the crucible by sucking the crucible dry after its first potassium chloride treatment, heating, cooling and again running 30 cc. of potassium chloride through the crucible as above. The two sets of blanks agreed to within 2 ohms in about 2300 ohms. The results indicate that the sludge adsorbs or occludes a negligible amount of electrolyte if any. The data follow.

TABLE 8.

Comparison of Gold-Electrolyte Ratios
Between Sols with and without Sludge

Sols without appreciable sludge			Sols with sludge		
Sol	Gold Content	Ratio Au : KCl	Sol	Gold Content	Ratio Au : KCl
56.	3.40×10^{-4}	43 : 1	57.	4.15×10^{-4}	48 : 1
37.	4.77	49 : 1	59.	5.20	45 : 1
58.	4.87	50 : 1	50.	6.20	41 : 1
42.	10.5	52 : 1	61.	10.3	48 : 1
43.	11.0	47 : 1	45.	11.1	43 : 1

TABLE 9.

Tests on Sludge

Sol	Cell	0.002 M KCl through sludge after heating	Blank
8.	70	1196 ohms	1197 ohms
			1195
9.	71	1198	1198
			1196
10.	71	1195	1195
			1197
14.	70	1196	1196
		0.001 M KCl through sludge after heating	
11.	71	2353	2354
12.	70	2355	2354
18.	70	2355	2353
19.	70	2354	2355

The Ratio Gold-Electrolyte on 0.001 M KCl-H_2O Bredig Sols.

Since preliminary data indicated that such measurements were substantially free from variables due to contamination, electrolysis, centrifuging and electrolyte losses due to sludge, a number of sols were next made in an attempt to measure the ratio of gold to electrolyte in Bredig sols made in 0.001 M KCl solutions. Each sol was centrifuged before measuring at about 1200 x gravity for one hour. Such sols do not give constant electrolyte values when measured immediately after formation but do apparently reach a steady state after standing a week to ten days; the time required depends on the gold content, increasing therewith. This ratio after the stable state is reached is surprisingly constant and varies little if any with the gold content, the time of arcing, or the electrical circuit, provided an arc of about the same size is maintained. A different ratio was obtained when a much larger arc was struck.

Table 10 records the results of such measurements on 39 sols.

TABLE 10..

Electrolyte-Gold Relationship

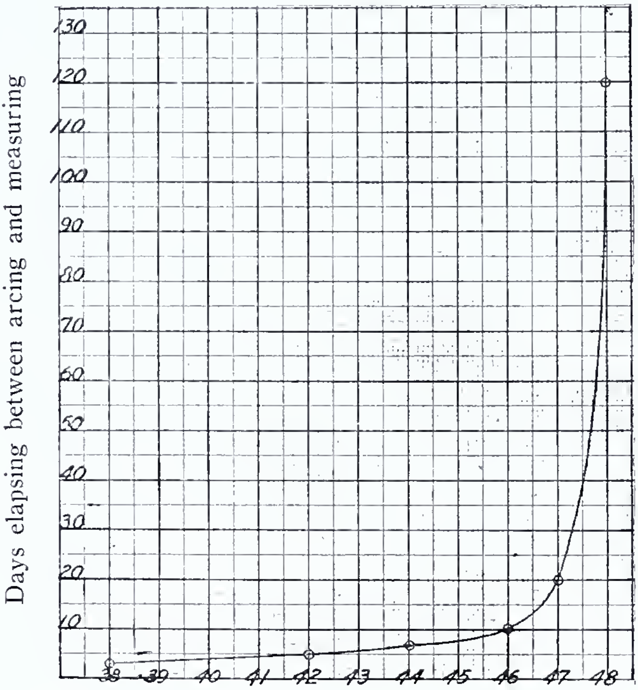
Sol	Electrical Circuit volts	ohms	m. f.	Time of Arcing minutes	Vol. cc.	Gold Content at. wts./l. x 10^{-4}	Chloride Removed m./l. x 10^{-5}	Time before Meas. days	Ratio Au : KCl
24.	110	40	1	60	250	6.10	1.37	1	44 : 1
25.	110	16	1	180	250	7.15	1.95	2	37 : 1
26.	110	16	1	30	300	5.64	1.29	3	44 : 1
27.	110	16	1	60	250	7.46	2.16	3	35 : 1
28.	110	16	1	60	300	10.3	2.34	3	39 : 1
29.	110	16	1	130	250	12.7	3.37	3	38 : 1
30.	110	16	1	180	250	13.5	3.97	3	34 : 1
31.	110	16	1	90	320	10.7	2.73	4	39 : 1
32.	110	16	1	120	200	11.7	3.08	4	38 : 1
33.	10	10	8	30	200	3.10	0.625	5	49 : 1
34.	110	16	0	30	200	4.10	1.04	5	40 : 1
35.	110	16	1	90	300	11.6	2.56	5	45 : 1
36.	110	16	1	90	200	15.3	4.61	5	33 : 1
37.	10	10	0	30	200	4.77	0.980	7	49 : 1
38.	110	16	0	30	250	4.97	1.37	7	36 : 1
39.	110	16	1	30	300	6.40	1.42	7	45 : 1
40.	110	40	1	120	175	8.00	1.04	7	40 : 1
41.	110	40	1	15	200	8.13	1.50	7	53 : 1
42.	110	16	0	75	250	10.5	2.00	7	52 : 1
43.	110	16	0	60	250	11.0	2.33	7	47 : 1
44.	110	40	1	30	250	11.0	2.30	7	48 : 1
45.	110	40	1	140	200	11.1	2.60	7	43 : 1
46.	110	16	1	180	250	11.4	3.10	7	37 : 1
47.	110	40	1	60	300	12.5	2.70	7	46 : 1
48.	110	40	1	60	160	16.2	3.56	7	46 : 1
49.	110	40	1	60	200	20.7	5.90	7	35 : 1
50.	110	40	1	30	250	6.20	1.50	8	41 : 1
51.	110	40	1	120	200	9.75	2.04	8	48 : 1
52.	110	16	1	15	250	5.48	1.25	10	44 : 1
53.	110	40	1	70	175	15.0	3.32	10	45 : 1
54.	110	16	1	60	200	15.3	3.20	10	48 : 1
55.	110	40	1	180	200	25.9	5.46	10	47 : 1
56.	110	16	0	15	250	3.40	0.875	21	43 : 1
57.	110	40	1	15	300	4.15	0.875	21	48 : 1
58.	10	10	0	Composite		4.87	0.960	120	50 : 1
59.	110	40	1	15	200	5.20	1.15	120	45 : 1
60.	110	40	1	Composite		9.05	1.88	120	51 : 1
61.	110	16	1	Composite		10.3	2.08	120	48 : 1
62.	110	16	1	Composite		11.8	2.46	120	48 : 1

Variation of the Gold-Electrolyte Ratio with Time.

The variation of the ratio with the time elapsing between manufacture and measurement is shown in Table 11 and graphically by Curve 2. In this table the ratio represents average values on at least 4 sols for each period elapsing between making and measuring. Sols varying in gold content from less than 100 mg. per liter to about 500 mg. per liter reach a state where the change of chloride ion with time is apparently negligible within periods of from about 7 to 10 days.

FIG. 2.

The influence of time on the ratio of Gold to electrolyte in Bredig Gold Sols. made in 0.001 M KCl-H_2O by an oscillatory arc.



$$\text{Ratio} = \frac{\text{Atomic Wghts. Gold}}{\text{Moles of KCl}}$$

TABLE 11.

Variation of Gold-Electrolyte Ratio with Time

Bredig Sols—0.001 M KCl—H_2O

Time elapsing between making and measuring	Ratio Au : KCl	Average value from
3 days	38 : 1	5 sols
5	42 : 1	4
7	44 : 1	13
10	46 : 1	4
10–120	48 : 1	7
120	48 : 1	5

Variations with Different Electrical Arcing Circuits.

As Svedberg has pointed out, the nature of Bredig sols varies to some extent with the electrical circuit employed. Amsden has made similar observations. Precise measurements on this phenomena were not attempted. It was observed, however, that by increasing the capacity in the circuit to 3 m. f. a much larger arc was obtained than when 1 m. f. or no capacity circuits were employed. As a matter of record the following comparisons are given showing sols made with varying electrical circuits. The ratio gold-electrolyte is an average value for all sols made with each circuit. The sols were measured 7 days or more after making.

TABLE 12.

Variation of Gold-Electrolyte Ratio with the Electrical Circuits Employed

Electrical Circuit			No. of Sols	Ratio Au : KCl	High	Low
volts	ohms	m. f.				
110	16	0	5	43 : 1	52:1	36:1
110	16	1	5	42 : 1	48:1	37:1
110	40	1	13	45 : 1	48:1	35:1
10	10	0	2	49 : 1	49:1	49:1
110	16	3	6	71 : 1	76:1	63:1

Variation with Gold Content.

It has previously been mentioned that the gold content affects the time required to come to the stable state. A more complete record of this effect is shown below where sols made and measured after definite periods are arranged according to their gold content.

Three series of sols are shown, namely those sols made with a 110 volt circuit. It will be noticed, as previously indicated, that differences in the ratio are not significant after the sols have stood long enough to reach stability, e. g. for more than 7 days.

TABLE 13.

Variation of Gold-Electrolyte Ratio with Gold Content

Electrical Circuit			Days	Gold Content	Ratio Au : KCl
volts	ohms	m. f.		at wts. 1. x 10^{-4}	
110	16	1	3	5.64	44 : 1
				7.46	35 : 1
				10.3	39 : 1
				12.7	38 : 1
				13.5	34 : 1
			4	10.7	39 : 1
				11.7	38 : 1
			5	3.10	49 : 1
				11.6	45 : 1
				15.3	33 : 1
110	40	1	7	11.0	48 : 1
				11.1	43 : 1
				12.5	46 : 1
				16.2	46 : 1
				20.7	35 : 1
			10	15.0	45 : 1
				15.3	48 : 1
				25.9	47 : 1
			21	3.40	43 : 1
				4.15	48 : 1
			120	5.20	45 : 1
				9.05	51 : 1
110	16	3	7	9.90	76 : 1
				10.3	67 : 1
				11.2	75 : 1
				11.7	71 : 1
				13.4	63 : 1

The above results are not considered as conclusive. Further study of this effect is needed. However, these results indicate an effect not previously noted and one to which the attention of future investigators should be directed.

Effect of Freezing.

Previous investigators have observed that freezing gold sols, aside from the precipitating effect first observed by Bredig[12], and later by Zsigmondy[44], also apparently changes the electrolyte concentration of the medium in which the sols are prepared.

Several sols were frozen in carefully protected non-sol bottles and a comparison of the apparent electrolyte content before and after freezing was made by conductivity measurements on the medium before arcing, on the sols, and on the clear liquid which results after the frozen sols are melted. The results show that some electrolyte is released to the medium upon precipitation by freezing. In no case did the medium return to its original conductivity. It is probable that occlusion of the electrolyte by the precipitated gold is largely responsible for that electrolyte which does not reappear. The results are given in Table 14.

TABLE 14.

Electrolyte Distribution in Bredig Gold Sols
Before Freezing

Compared with the Mother Liquor
After Freezing

Sol	KCl before freezing	KCl after Freezing	Original KCl
26.	98.7 x 10^{-5} m./l.	99.5 x 10^{-5} m./l.	100.0 x 10^{-5} m./l.
27.	97.8	98.6	"
35.	97.4	98.5	"
60.	98.5	99.7	"
61.	97.9	99.6	"
62.	97.5	99.5	"

Effect of Boiling.

To throw further light on the nature of this Bredig gold colloid, certain sols were next subjected to a refluxed boiling operation for varied times up to one hour. Svedberg and others have previously concentrated Bredig sols by evaporation. No observations on the effect of prolonged heating under substantially constant conditions have previously been made, however, and the stability of the sol under such conditions should help indicate its nature since it is known that mere absorption usually decreases with the continued application of high temperature digestion.

A reflux condenser of Pyrex glass was employed. The condenser was cleaned, rinsed with conductivity water and allowed to drain for ten minutes. Connection to a flask containing conductivity water was then made and the water boiled, the flame removed, and draining allowed to proceed for five minutes. The flask containing the sol was then substituted for that containing the water, after first removing a portion of the sol to a conductivity cell. The sol was boiled for the desired time, boiling stopped, drained for five minutes and the conductivity again measured. It was found that a blank comprising 0.001 M KCl solution treated as previously described gave the same conductivity before and after boiling. The results on KCl and sols are given in the table below.

TABLE 15.

The Effect of Boiling Bredig Sols Under Constant Conditions

		Resistance in Ohms			
	Cell	Before Boiling	15 min. Boiling	30 min. Boiling	60 min. Boiling
KCl—0.001 M	70	2372	2372	2371	2372
	71	2374	2375	2374	2375
Sol 42	70	2409	2408	2408	2408
	71	2410	2409	2408	
Sol 44	70	2417	2417	2418	
	71	2421	2420	2422	2421
Sol. 48[++]	70	2188	2187	2194	2186
	71	2190	2191	2195	2188

[++] This sol was contaminated during arcing and was reddish purple. Its color did not change on boiling.

The colloid is apparently stable, even when boiled, and shows no substantial change in its composition. A faint yellow gold color could be seen on the bottom of the flask after boiling.

Thus far the work done had been different from that of previous investigators in several respects, the more important of which were:

1. The method of arcing was modified.
2. The variables in the system were more rigidly controlled.
3. The method of measuring the sols, namely conductivity, had not previously been tried as a means of estimating the electrolyte portion of the colloid.

Since any one of these differences might prove a source of considerable variation, it is instructive to compare results obtained here with those of former investigators whose work had been done in systems where the variables had also been controlled. The table below records evaluating data. To make results more readily comparable, the results of all investigators, which have previously been reported in varying terms, have been reduced to a common denominator, values for which are given in the last column of the table.

TABLE 16.

Comparison of Gold-Electrolyte Ratio in Bredig Aqueous Sols as Obtained by Several Investigators

Author	Method of Measurement	Type Arc	Gold Content at. wts./l. x 10^{-4}	Electrolyte	Ratio-Gold Electrolyte
Beaver	Conductivity titration	D. C.	6.4	NaOH 0.005 M	27 : 1
			15.3	NaOH 0.001 M	26 : 1
			19.6		33 : 1
			9.4	HCl 0.0011 M	41 : 1
			19.3		34 : 1
			20.8		16 : 1
Shear	AgCl Electrodes Potentiometric	D. C.	193.0	KCl 0.001 M	51 : 1
Amsden	AgCl Electrodes Potentiometric	A. C.	13.4	KCl 0.001 M	13 : 1
			31.0		14 : 1
			44.2		10 : 1
			extrapolated to 0 gold	KCl 0.0003 M	47 : 1
			33.3		33 : 1
			40.6		29 : 1
Layton	Potentiometric One electrode out of medium		13.4	KCl 0.0014 M	33 : 1
			29.3	KCl 0.0013 M	42 : 1
			64.2	KCl 0.0014 M	52 : 1

From Table 16 it is apparent that Beaver, Shear and Layton working with different systems and different methods of measurement arrived at remarkably similar results. Beaver's average for the gold-electrolyte ratio is 37 (the last sol in the table has not been included since Beaver clearly shows that sols of high gold content cannot be precisely measured); Shear obtained a value of 51 : 1; Layton's average is 42 : 1. Amsden's value of 12 : 1 for 0.001 M KCl is apparently low. His average for 0.00037 M KCl is 36 : 1, however, and compares favorably with the values of Beaver, Shear and Layton.

For the purpose of further reducing all variables to a common denominator where possible, it was then decided to carry the present investigation onward and repeat measurements modelled after Beaver on the one hand, and Shear, Amsden and Layton on the other.

Conductivity Titrations.

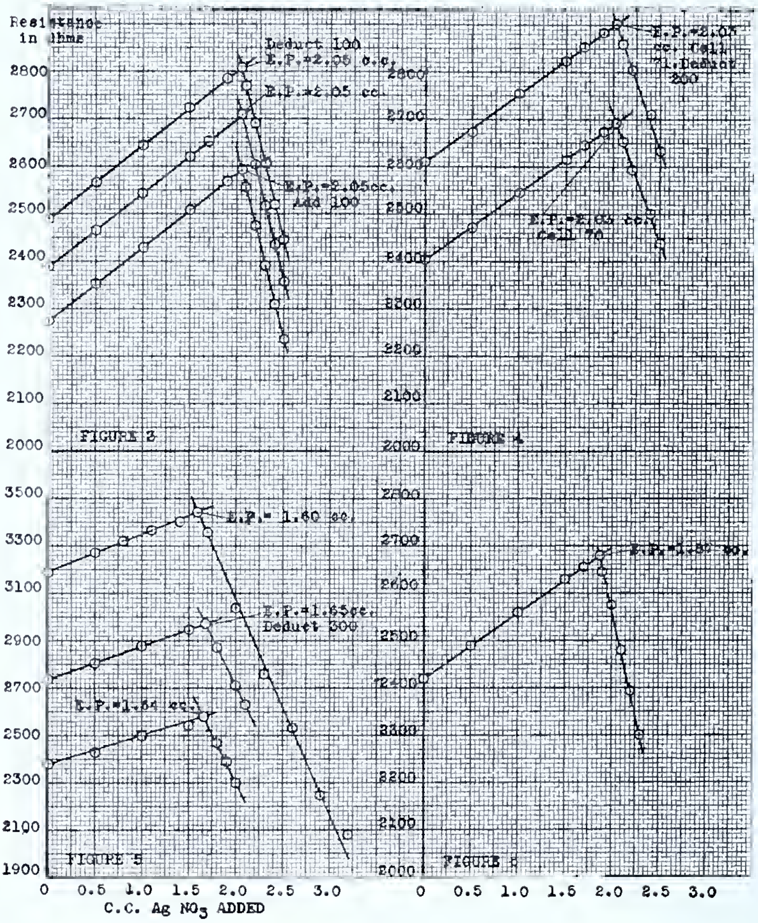
The sols employed for these measurements were made and centrifuged as previously described.

The measuring circuit and cells employed have also been described. In addition, a 5 cc. burette of the Folin[15] type with a very fine tip, and graduated to 0.01 cc., was calibrated. No difficulty was experienced in gauging its flow to 0.002 cc. The cell was protected with a cotton plug during the addition of the titrating agent.

C. P. silver nitrate recrystallized from conductivity water was then made up to an approximately 0.1 M solution and standardized by Mohr's[16] method against potassium chloride purified as previously described. This solution was diluted to its final value of about 0.01 M with calibrated pipette and a liter flask, also calibrated.

The potassium chloride solutions before arcing were titrated with the silver nitrate solution and the sols made therein similarly titrated and compared therewith to find the electrolyte changes coincidental with sol formation. The usual graphical method of Dutoit and Kolthoff[17] was employed to ascertain the end point, i. e. extension of the straight lines obtained on both sides of the stoichiometric point. Beaver[25], Pauli and Fuchs[18], Beaver and Muller[49] and Pennycuick[31] have previously employed this method for studies on colloidal sols similar to those studied here.

The Conductimetric Titration of KCl and Sols 58, 61 and 68 With 0.00975 M $AgNO_3$. T= 25 ± 0.002° C. Freas Cells, Bare Platinum Electrodes



Determinations were made in duplicate. The cells were continually immersed in the thermostat and were given ten minutes to come to equilibrium after the addition of silver nitrate and vigorous shaking.

The chief difficulty with this method lies in the fact that the conductivity of the sols drifts as they are titrated; the more gold the sols contain, the more uncertain the results are on account of pronounced driftage which makes reading very uncertain. Beaver observed and recorded a similar difficulty. Sols of gold content much over 500 mg./liter cannot, in fact, be titrated at all since they precipitate during titration. This phenomenon is probably due to the removal of chloride ion or to the formation of insoluble silver chloride at the gold-water interface.

The data are given in the preceding curves and tables below.

TABLE 17.

Titration of 0.001 N KCl with 0.00975 N $AgNO_3$

20 cc. 0.001 N KCl	Resistance in Ohms			
cc. $AgNO_3$ added	Cell 70		Cell 71	
0.00	2392	2376	2391	2381
0.50	2468	2453	2466	2457
1.00	2546	2530	2544	2534
1.50	2624	2609	2622	2616
1.70	2656	2640	2653	2642
1.90	2684	2669	2681	2672
2.10	2670	2655	2680	2661
2.20	2592	2576	2607	2583
2.30	2504	2492	2519	2497
2.40	2420	2410	2438	2414
2.50	2345	2335	2358	2340

End point = 2.05 cc.

TABLE 18.

Titration of Sol 58 with 0.00975 N $AgNO_3$

20 c.c Sol 58	Resistance in Ohms	
c.c. $AgNO_3$ added	Cel 70	Cell 71
0.00	2410	2406
0.50	2474	2472
1.00	2555	2547
1.50	2623	2618
1.70	2654	2645
1.90	2683	2675
2.10	2661	2652
2.20	2605	2594
2.40	2511	2502
2.50	2433	2439

End Point = 2.03 c. c.

KCl removed by sol = 0.975×10^{-5} m./l.

Au in sol = 4.87×10^{-4} m./l.

Ratio Au : KCl = 50 : 1

TABLE 19.

Titration of Sol 61 with 0.00975 N $AgNO_3$

20 c.c. Sol 61 c.c. $AgNO_3$ added	Resistance in Ohms Cell 70	Cell 71	
0.0	2449	2382	3193
0.50	2507	2444	3270
0.80			3327
1.00	2581	2499	
1.10			3364
1.40			3401
1.50	2648	2546	
1.60		2548	
1.70		2538	3359
1.80	2577	2477	
1.90		2391	
2.00	2411	2305	3042
2.10	2331		
2.30			2767
2.60			2538
2.90			2247
3.20			2080
3.50			1949

This sol drifted during the period of measurement and the gold precipitated.

End point = 1.62 c. c.
KCl apparently removed = 21.4 x 10^{-5} m./l.
Au in sol = 10.1 x 10^{-4} m./l.
Ratio Au : KCl = 5 : 1

TABLE 20.

Titration of Sol 68 with 0.00975 N $AgNO_3$
Showing Driftage

20 c.c. Sol 68 c.c. $AgNO_3$ added	0 min.	5 min.	Resistance in Ohms 10 min.	15 min.	20 min.	30 min.
0.00	2419	2419	2419	2419	2419	
0.50	2491	2487	2487	2487		
1.00	2560	2560			2561	
1.50	2631	2632	2632			
1.60	2644	2644	2643			
1.70	2654			2651		
1.80	2656			2654		2654
1.90	2645			2642		2639
2.00	2576			2569		2568
2.10	2483			2481		2478
2.20	2395			2393		2383
2.30	2302					2298

Aside from the driftage shown above, these sols continue to drift over considerable periods of time. The titration at 2.30 for example, reaching a value of 2286 at the end of an hour.

End Point = 1.87 cc.
KCl removed by sol = 8.78 x 10^{-5}m./l.
Au in sol = 111 x 10^{-5} m./l.
Ratio Au : KCl = 13 : 1

These results clearly indicate the same trends shown by Beaver. Conductivity titration is especially suited for use with sols having a small gold content. As the gold content increases, the results are obscured by precipitation and probable concomitant adsorption of the titrating reagent. For sol 58, the results check those obtained by conductivity, as a comparison of the above values with the conductivity values for the same sol as given in Table 10 show.

Potentiometric Measurements.

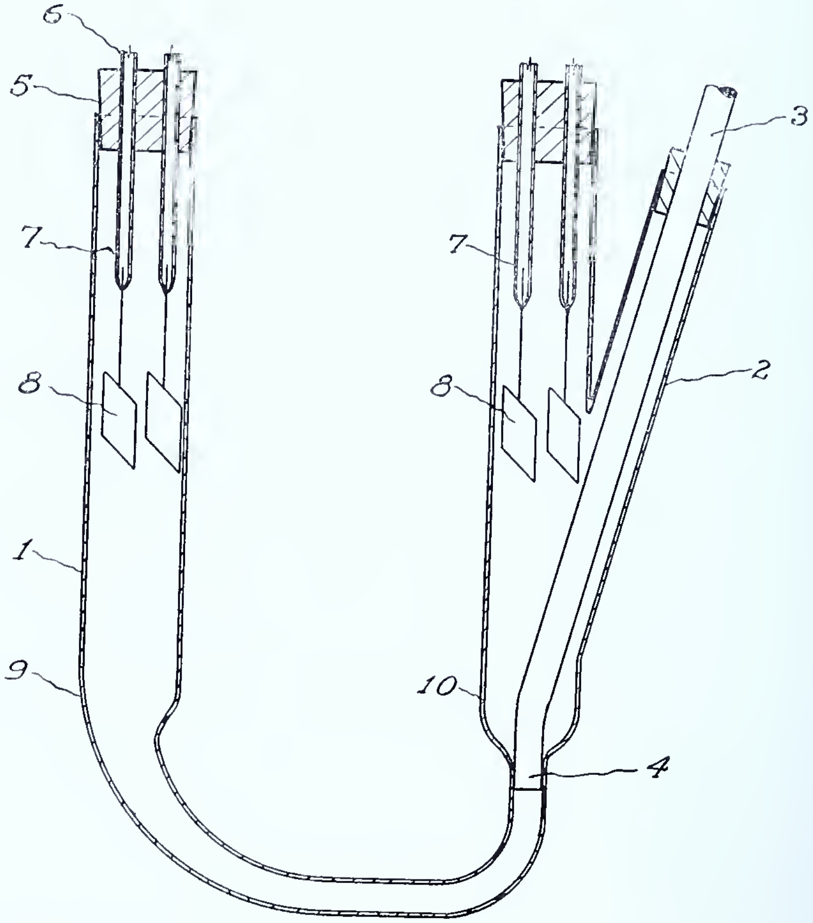
Sols from the foregoing series were next measured after the method of Shear, Amsden and Layton who used the system Ag—AgCl—Sol : 0.005 M KCl—AgCl—Ag to determine experimentally the chloride ion activity before and after sol formation. The method used by these investigators was not substantially changed, but a new working cell was designed to facilitate handling and reduce the likelihood of contamination.

This cell in which the E. M. F. measurements were made is shown in Fig. II. Referring to the drawing, 1 is a modified Pyrex glass U tube with arms 9 and 10 and a side arm 2 through which an elongated glass stopper 3 passes into the tube and effects a ground glass closure at 4. Glass stoppers 5 introduce glass tubes 6, terminating in sealed in platinum wires 7 and silver chloride electrodes 8 which dip into the solutions to be measured. The tubes 6 contain mercury and wires lead thence to the potentiometric circuit.

In operation the cell and stopper are first cleaned, then thoroughly rinsed with water, distilled water and conductivity water. After vigorous shaking to remove most of the water, the stopper 3 is put in place and arm 9 is rinsed several times with small portions of the sol to be measured, taking care to tilt the apparatus so that all the air near 4 is displaced. Arm 10 is then thoroughly rinsed with 0.005 M KCl. Arm 9 is now filled with the sol to a point above that

FIG. II.

Cell for Measuring the E. M. F's



to which electrodes 8 extend. All air must be displaced. Arm 10 is similarly filled with 0.005 M KCl. The electrodes are set in place and the cell submerged in a thermostat so that the liquid within the cell is below the surface of the thermostat liquid. The cell is allowed to come to temperature for fifteen or twenty minutes. The solutions may be stirred from time to time with electrodes 8. Stopper 3 is then slowly and carefully withdrawn from 4. The two solutions from 9 and 10 form a sharply defined liquid junction near 4. Provided the cell is kept reasonably quiet no observable mixing takes place over a period of a week or more. The stopper should be pushed along 3 and put in place to prevent possible contamination from the air. If this cell is used with liquids of different specific gravity, it is advisable to put the heavier liquid in arm 9.

The cell is simple in handling, easy to clean and practically free of all contamination difficulties. Sharp boundaries between the solutions to be measured are readily obtained. As an additional safety factor in case both solutions are colorless, the electrodes should terminate well above the bend in the U tube.

It will be noted that the static junction here chosen is satisfactory since the migration velocity of potassium and chloride ions is substantially the same.

The silver chloride electrodes were placed in pairs in each half cell after the procedure described by Shear. These electrodes, made by the process of McInnes and Beattie[50], consisted of squares of 35 mesh, 22 gauge platinum wire 2 cms. on edge. They were silver plated for 24 hours in 10% $KAg(CN)_2$ using a current of 3 milliamps. The direction of the current was reversed at the end of 12 hours and the electrodes plated in pairs. The electrodes were washed in water and dilute hydrochloric acid and heated to faint redness.

Silver chloride coatings were obtained by making these electrodes the anodes in a 0.05 M KCl solution and electrolyzing for 15 minutes with a current of 7 milliamps. After washing in water and 0.005 M KCl, the electrodes were placed in 0.005 M KCl and allowed to soak while short circuited for 24 hours before using. As a general rule, the difference between individuals of any set of four electrodes so prepared is 0.1 m. v. or less. Sets checking to 0.05 m. v. or less were frequently obtained. Any set of four electrodes to be used for measurements was always checked immediately prior to use.

As a further check on the cell, electrodes and working circuit, the potential of 0.005 M KCl—0.001 M KCl was measured at 25° C. with a set of four such AgCl electrodes. These electrodes in 0.001 M KCl gave the following observed differences:

1A—1B	0.00 m. v.
2A—2B	0.01 m. v.
3A—3B	0.01 m. v.
6A—6B	0.02 m. v.

The following potentials were observed when sets 1 and 2 were placed in 0.001 M KCl and 0.005 M KCl respectively and the stopcock removed from the cell.

1A—1B	39.33 m. v.	Av. 39.37 ± 0.05 m. v.
1A—2B	39.35 m. v.	
2A—1B	39.40 m. v.	
2A—2B	39.40 m. v.	

After washing and refilling the cell:

1A—1B	39.40 m. v.	Av. 39.42 ± 0.05 m. v.
1A—2B	39.40 m. v.	
2A—1B	39.45 m. v.	
2A—2B	39.45 m. v.	

With fresh KCl and sets 3 and 6 the following values were obtained:

3A—6A	39.50 m. v.	Av. 39.45 ± 0.05 m. v.
3A—6B	39.50 m. v.	
3B—6A	39.37 m. v.	
3B—6B	39.45 m. v.	

The potential of the cell KCl 0.005 N—KCl 0.001 N at 25° C. may be calculated from the usual Nernst formula as modified to include activity coefficients after the manner of G. N. Lewis[51]. Accepting the value of (Cl^-) in 0.001 N KCl as 0.977 and in 0.005 N KCl as 0.923 as given by Noyes and McInnes[52], the calculated potential after due allowance for the slight difference of migration velocity of K^+ and Cl^-[53], is

$$E = 0.0590 \times 0.992 \times \log \frac{0.005 \times 0.923}{0.001 \times 0.977} = 39.47 \text{ m. v.}$$

This value compares favorably with those obtained above, the average difference being of the order of 0.1 - 0.2% and is taken to indicate a satisfactory cell and electrode performance.

Measurements were next made on sols by employing the above cell as follows:

Ag—AgCl—Sol : 0.005 N KCl—AgCl—Ag

It was found that measurements reproducible to 0.1—0.3 m. v. can be readily made, i. e. with a precision practically one significant figure beyond those made by Amsden and Shear. The readings are steady within a few tenths millivolt for periods even up to 24 hours and do not show the pronounced driftage observed by Shear. Results are given below to show in detail the values obtained from two typical sols.

E. M. F. Measurements on

Ag—AgCl—Sol : KCl (0.005 N)—AgCl—Ag

Sol. 61	Electrodes—No. 2 in sol, No. 1 in KCl (0.005 N)		
5/17/29	2A—1A	44.80 m. v.	
	2A—1B	44.82	
	2B—1A	44.78	
	2B—1B	44.80	
	Cell refilled and electrodes checked		
5/19/29	2A—1A	44.92 m. v.	Av. 44.89 ± 0.02 m. v.
	2A—1B	44.90	
	2B—1A	44.90	
	2B—1B	44.85	
	After 15 hours in the thermostat		
	2A—1A	44.90 m. v.	Av. 44.86 ± 0.03 m. v.
	2A—1B	44.87	
	2B—1A	44.85	
	2B—1B	44.80	
Sol 58	Electrodes—No. 1 in sol, No. 6 in KCl (0.005 N)		
	1A—6A	40.30 m. v.	Av. 40.33 ± 0.03 m. v.
	1A—6B	40.35	
	1A—6A	40.30	
	1B—6B	40.37	
	Electrodes—No. 1 in KCl, No. 2 in sol		
	1A—2A	40.40 m. v.	Av. 40.37 ± 0.02 m. v.
	1A—2B	40.35	
	1B—2A	40.37	
	1B—2B	40.35	

Similar measurements were made on several other sols. The results obtained are summarized in Table 21.

TABLE 21.

Summary of E. M. F. Measurements

on the System

Ag—AgCl—Sol : KCl (0.005 N)—AgCl—Ag

Sol	Period elapsed between Making and Measuring days	Observed Potential m. v.	Gold Content m./l. x 10^{-4}	(Cl^-) in Sol x 10^{-4}	Loss in (Cl^-) x 10^{-5}	Ratio Au : (Cl^-)
58.	120	40.40	4.87	9.42	3.3	14 : 1
60.	120	44.60	9.05	7.98	17.9	5.1 : 1
61.	120	44.80	10.3	7.92	18.5	5.6 : 1
62.	120	44.75	11.8	7.94	18.3	6.5 : 1
24.	1	45.00	6.10	7.88	18.9	3.2 : 1
50.	8	43.70	6.20	8.27	15.0	4.1 : 1
68.	120	42.36	11.1	8.72	10.5	10.5 : 1

The first four sols in the above table are strictly comparable, having been made under substantially the same arcing conditions and measured after the same period of time had elapsed. Sols 24 and 50 were measured before sufficient time had elapsed for a steady state to become completely established. Sol 68 belongs to the series of sols which were made with a 3 m. f. arc and which as previously shown gives a distinctly higher ratio of gold to chloride, probably because the particles are larger in size.

In the above summary, the results recorded in the third column as observed potentials in millivolts represent an average of from 16-20 measurements on each sol. The measurements were in general made with different sets of electrodes and in the larger part agreed within ± 0.1 m. v.

It seems that there are three significant facts apparent from the data in this table. (1) Sols of small gold content, after having reached equilibrium, give higher values for the ratio of [Au] : (Cl^-). These observations agree in trend with those reported by Amsden, and likewise agree in trend with those obtained by conductivity and conductivity titration. (2) The further a sol is from a steady state, i. e. the shorter the time which has elapsed between its making and measuring, the greater the gold content appears to be in relationship to the chloride ion removed. This trend is also like that observed in measurements by conductivity. (3) The same significant difference in the ratio of gold to electrolyte obtained when the arcing circuit is changed to produce a richer arc appears both in conductivity measurements. The ratio of gold to electrolyte removed is larger.

It cannot be said that these results check those obtained by Amsden, but the order of magnitude is certainly very much the same, as are also the observable trends. Thus Amsden obtained for a sol containing 13.4×10^{-4} moles per liter, a ratio of 13.4 : 1 for the [Au] : (Cl^-), which value decreased to 5.5 : 1 for a sol containing 31.9×10^{-4} moles of gold per liter.

It will be noted that there is a very substantial difference in the ratio [Au] : [Cl^-] and that of [Au] : (Cl^-) obtained respectively by conductimetric and potentiometric measurements. This phenomenon is believed to be due to the probability that conductivity measures only such chloride ions as are actually bound to the gold particles and contribute to the actual colloidal complexes, while activity measurements represent the sum total loss of both chloride ions forming the colloid and also those in the solution external thereto but sufficiently near by to become loosely aggregated or bound, and hence in part inactivated. This phenomenon will be discussed in greater detail later.

Discussion.

From a theoretical viewpoint, the previously reported data may give rise to several interesting possiblities. In a discussion of these it is interesting to consider what inferences can be drawn concerning the size, charge and potential of the particles. It is also instructive to compare such values as can be obtained from the data in hand with results which have been reported by other investigators which, of course, serves to evaluate, to some extent at any rate, the probability of the correctness of the assumptions which are necessarily involved in computations of this nature.

There is a notable difference between the results which have been obtained potentiometrically both by Amsden and in this investigation, and those which have been obtained by conductimetric measurements. It is believed that these differences can be satisfactorily accounted for and such considerations will occupy the second phase of this discussion.

As for the nature of the colloid itself and its relationship to the medium in which it exists, this has been the source of considerable speculation, and several theories have been advanced to account for its formation, behavior and destruction. To this question, the final portion of this discussion will be devoted.

The Charge and Size of the Particle.

Layton[29] is the originator of a very interesting method of calculating the charge and size of Bredig gold particles. He has assumed that the particle is spherical. It will be noted that this assumption is not without a fairly substantial experimental basis, as shown by Svedberg and others. Moreover, similar assumptions have been made by practically all others who have attempted to make calculations in this field and are reasonable because the method of manufacture involves the production of gold vapor and condensation thereof through the liquid to the solid state. It is known that liquid metals have exceedingly high surface tensions and therefore would expectedly take the form of lowest energy, namely droplets[54, 55].

Layton has further assumed that the minute gold spheres so formed act as condensation nuclei upon the surface of which chloride ions gather in sufficient numbers to completely cover and pack the surface. The validity of this assumption cannot be proven but can be evaluated by comparison with other measurements. It is known, however, that measurable chloride ions disappear when Bredig colloidal gold solutions are formed which, unless they be associated with the gold, practically cannot be accounted for. It is also known that gold forms one of its most stable chemical compounds with chloride ions.

Based on the results which he obtained by producing colloidal Bredig gold with an arc one electrode of which was external to the solution, which therefore could not possibly permit electrolysis, and on the above assumptions, Layton measured the chloride ion used up coincidentally with sol formation and calculated the size of and the charge on the particles. In the present investigation a different method of making sols has been employed and a different method of measuring the chloride ion apparently bound up in the formation of the colloid. It is therefore interesting to see what values of particle size and charge one obtains on the basis of the present measurements and Layton's assumptions. The calculations are based on conductimetric measurements as shown in Table 10.

As illustrative of values obtainable, sol 58 may be considered as representative and a calculation based on the data therefrom follows.

Sol 58

Chloride ions apparently bound to the gold are

(1) $6.06 \text{ x } 10^{23} \text{ x } 0.960 \text{ x } 10^{-5} = 5.73 \text{ x } 10^{18}$ ions/liter.

The area occupied by these chloride ions is

(2) $5.73 \text{ x } 10^{18} \text{ x } (3 \text{ x } 10^{-8})^2 = 5157$ sq. cm.

The number of gold particles required to give such an area is

(3) $\dfrac{5157}{4\pi r^2}$

but this number of spheres has a weight of 96 mg. Hence the weight of a single particle equals

$$(4)\quad \frac{0.096}{\frac{4\pi r^2 \times 19.3}{3}}$$

Equating and solving for r, the value of the radius is 2.9×10^{-6} cm.

For the radius of such particles, Layton obtained a value of 3.1×10^{-6} cm; Pauli and Adolf[56], from the ultramicroscope and on the assumption of a cubical particle, reported a value of 2.6×10^{-6}, Pauli and Fuchs[48], a value of 2.9×10^{-6} and Svedberg and Inouye[57] give a value of 2.7×10^{-6}.

Proceeding in a similar fashion and following Layton, the number of particles per liter is found from Equation 3 to be 4.88×10^{13} while the number of ions per particle equals, from Equation 1, 1.2×10^{5}. For comparison, Pauli and Adolf[56] report 5.7×10^{4}, and Pauli and Fuchs [48] 4.6×10^{4} ions per particle.

From this the charge per particle in electrostatic units equals

$$(5)\quad 1.2 \times 10^{5} \times 4.77 \times 10^{-10} = 5.7 \times 10^{-5}$$

Layton obtained a value of 6.4×10^{-5} e. s. u. while other investigators have give various estimates ranging from 8×10^{-8} to 2×10^{-2} [58]. This charge, in all probability, does not represent the effective charge of the colloidal aggregate as a whole since the chloride ions would operate to attract oppositely charged ions, i. e. K^+, which in turn will produce a reduced effective charge, that is the colloid as a whole will be less highly charged with respect to its environment. Any actually measured charge, it may reasonably be supposed, corresponds to the charge of the aggregate and not to that calculated above which considers only gold and Cl^-.

The Potential Colloid v. External Solution.

In a discussion of the potential which exists between colloidal surfaces and the solution which is in contact therewith, Freundlich[59], after pointing out that the relationship involving potential is not simple, goes on to state that at least a portion of the curve representing the relationship may be adequately characterized by the equation

$$\text{P. D.} = K \times \log \frac{Y}{c}$$

where K and Y are constants and c is the concentration of the electrolyte. It is here proposed to show that for Bredig sols in aqueous potassium chloride solutions, this equation may take the more usual form and may be expressed as

$$\text{At } 25^\circ \text{ C., P. D.} = 0.059 \times \log \frac{c_1}{c_2}$$

where c_1 is the "effective" chloride ion concentration associated with the gold and acting as if uniformly distributed in a volume immediately in the neighborhood of the gold particles, and c_2 the chloride ion concentration in the solution at a point sufficiently far removed from the colloid so that the ionic distribution is uniform.

From the calculations previously given, we have already evaluated the number of chloride ions associated with the gold. This number of chloride ions was found to be 1.2×10^5. Now we may represent the system in the following schematic fashion:

	A		‖	B	
	Cl^-	K^+	‖		
Au	Cl^-	K^+	‖	K^+	Cl^-
	Cl^-	K^+	‖		
	Cl^-	K^+	‖		

The double line represents the outer edge of the volume within which the chloride ions represented in A may be considered as if forming one half of a concentration cell. The magnitude of this distance is unknown but may be very roughly approximated.

Smoluchowski[61, 62] from a statistical consideration of precipitation came to the conclusion that the sphere of attraction immediately surrounding colloidal gold particles should be twice the particle radius. His hypothesis was reasonably well confirmed by Westgren and Reitstotter's measurements on precipitation. They found this radius of attraction to be two to three times the particle radius. As a working hypothesis, it will be assumed here that Smoluchowski's hypothesis is valid and the radius of the sphere in which the chloride ions closely associated with the gold function, is the diameter of the gold particles upon which they are bound. It is interesting to note that Gouy[60], from a different angle, namely consideration of the Helmholtz double layer phenomena, calculates for particles of the size apparently in question here and in 0.001M electrolyte solution that the thickness of the double layer is 10^{-6} cm. In other words, the distance from the chloride ions associated with the gold to uniform distribution closely approximates that chosen here.

Now the volume of such a sphere is equal to

$$(1)\quad \frac{4\pi r^3}{4} = \frac{4\pi}{3}\,(2 \times 2.9 \times 10^{-6})^3 \times 10^{-3} = 7.8 \times 10^{-19} \text{ liters}$$

While the moles of chloride ion functioning therein is the number of chloride ions per particle divided by the number of chloride ions in one mole, i. e.

$$(2)\quad \frac{1.2 \times 10^{5}}{6.06 \times 10^{23}} = 0.198 \times 10^{-18}$$

Therefore the apparent concentration of chloride ions in A above is from Equations 1 and 2

$$(3)\quad \frac{0.198 \times 10^{-18}}{0.78 \times 10^{-18}} = 0.25 \text{ moles/liter}$$

In other words, the chloride ions immediately associated with the gold are the more concentrated half of a concentration cell. The other half of the cell contains as measured by conductimetric determinations, 9.9×10^{-4} moles of chloride ions per liter. From this and the Nernst formula given above, the potential existing between the two halves of the cell, i. e. between the charged gold particles and the solution which bathes them is

$$(4)\quad E.\,M.\,F. = 0.059 \log \frac{c_1}{c_2} = 0.59 \log \frac{0.25}{9.9 \times 10^{-4}} = 142 \text{ m. v.}$$

So far as known, no computations of the potential of such a system as described herein have been attempted, but different investigators have assigned values up to 105 m. v. for the potential existing in less stable systems than this[64, 65, 66].

To pursue this idea further, Beans and coworkers have repeatedly found all attempts to make a stable colloid are fruitless if the concentration of electrolyte in the original solution exceeds 0.01-0.02 M. As a possible explanation for this phenomenon, it will be noted that if the value of c_2 in Equation 4 increases to 0.02 M, the potential drops to 65 m. v. on the assumption that we would have there particles of substantially the same dimensions as those here involved.

The value of 65 m. v. which might be termed the critical potential, the terminology which is employed by Freundlich[67] to denote the potential below which the particles precipitate when electrolyte is added, is somewhat higher than that indicated by Freundlich as lying between 40 and 50 m. v. It is interesting to note that Whitney and Blake obtained a value of 58 m. v. for the potential gold sol in "pure" water.

Comparison of Activity and Conductivity Measurements.

Referring back to the experimental determination of the apparent concentration of chloride ions which remained measurable after colloid formation as determined by conductivity on the one hand, and the silver chloride electrode potentiometric system on the other, the following table shows that the chloride ion disappearing is considerably greater in the latter case.

TABLE 22.

Chloride Ions Associated with the Colloid

Sol	Gold Present as Colloid	Loss in Cl$^-$ By Conductivity	Loss in (Cl$^-$) By AgCl Electrodes
58.	4.87×10^{-4} m./l.	0.96×10^{-5} m./l.	3.3×10^{-5}
60.	9.05	1.88	17.9
61.	10.3	2.08	18.5
62.	11.8	2.46	18.3

As a mechanism for explaining these differences, it is here assumed that as stated by Svedberg[68] and McBain[8], the colloid behaves as a large ion with a rather large charge. Now such experimentation as has been done indicates that as ionic concentration increases, inactivation proceeds more rapidly than loss of mobility. In other words, conductivity gives values which lie closer to concentration than do activity measurements. This effect is magnified by introducing multivalent ions into the system. If, in the present system, the colloid behaves as a multivalent ion, its inactivating effect on the chloride ions in the same solution should give rise to higher values for chloride ion losses. The facts are plainly indicated by a comparison of sol 58 with sols 60, 61 and 62.

It might be possible to throw more light on the validity of the above assumptions were we able to make use of the Debye-Huckle theory for example, as applied by Bronsted and LaMer[69], which enables one to evaluate the activity coefficient of an ionic species provided the valence of each of the ions present is known and provided the distance of closest approach of ions one to the other may be evaluated. But here while we can measure the activity, we cannot measure the activity coefficient, and although we might assume that the concentration of the chloride ions is more accurately measured by conductivity, we still have no sufficient basis for determining the valence of the colloid because, though the charge thereon is evaluated, its effective valence cannot be so simply arrived at because of the screening effect of the potassium ions associated therewith.

And finally we may consider that puzzling question, the nature of Bredig sols. Bredig[12] himself, Burton[10], Zsigmondy[70, 71] and others[72] held for many years the view that the colloid was best formed by suspension in water, and such viewpoint had its firm adherents even after 1915 when Beans and Eastlack were able to show conclusively that gold does not form a colloid in pure water, but requires the presence of small amounts of stabilizing electrolyte and moreover, that only such electrolytes as form stable compounds with gold function as stabilizing agents. The facts there established are, according to Pauli and Eirich[74], without flaws.

At the present time, there are several theories which, with greater or less modification, have their supporters. Briefly stated, Zsigmondy[73] apparently believes that the colloid is substantially a gold nucleus which physically adsorbs hydroxyl ions presumably because of the large surface due to its small size and porosity. Pauli believes that the colloid particles comprise a gold nucleus, the surface of which consists of complex negatively charged gold chloride ions, $AuCl_4^-$ when the sol is made up in chloride solutions, and of complex negatively charged gold hydroxide ions, $Au(OH)_4^-$, in hydroxide solutions, with a surrounding layer of positive contra ions. These contra ions may be hydrogen ions or metallic ions such as potassium ions. The entire micelle, to employ the term used by Duclaux, Pauli and Eirich[74] picture as a Werner complex.

Beans and coworkers have developed a descriptive mechanism which postulates small particles of metallic gold, the surface of which presents an unsaturated field of force unique to gold which is capable of binding such ions as combine with gold in a stable associated group. There is thus a crystalline gold nucleus, a surface of gold and bound chloride ions and external or adjacent thereto, a layer of water molecules. Potassium or other cations surround the particle and electrolyte, e. g. K^+ and Cl^-, are external thereto. Wilson has developed a similar picture.

Before considering the relative merits of the different points of view, it is well to review the experimental facts. While it is not to be claimed that any theory is a complete and exhaustive picture and not subject to modification as new facts present themselves, it should also be emphasized that theories which do not accord with the facts are treacherously founded. Now gold is an element which shows two valences and which readily forms complex compounds[75]. It takes part in several catalytic chemical reactions and is particularly so used when finely divided to present a large surface[76]. Bredig gold sols cannot be formed in pure water[13]. In this respect they differ markedly from platinum, the oxides and oxyacids of which are stable chemical individuals[33]. Gold does not directly combine with oxygen so far as is known; one of its most stable compounds is gold chloride[75]. Careful analysis has failed to show any appreciable oxygen in residues from colloidal gold solutions[77]. There is no evidence that the chlorides of gold adhere to or unite with the metal. A stable Bredig colloid can be made by dispersing gold in conductivity water and thereafter adding chloride ions, the addition being made while no electric current is in any way associated with the process[26]. A stable colloid can be made by volatilizing gold in nitrogen by means of an arc and sweeping the vapor into the solution[78]. A stable colloid also results when gold is dispersed while having one electrode within and one outside of the solution in which the sol is produced[29]; under these conditions electrolytic decomposition of the stabilizing agent is impossible.

It is known that electrolysis invariably accompanies formation of Bredig gold sols when D. C. arc is employed, but measurements have also shown that electrolysis alone is insufficient to account for the chloride ion removed as the colloid forms[28]. When alternating current is employed, neither a chemical test with starch and iodine, nor a test with a conductivity cell indicates the formation of any appreciable chlorine, yet the sols so formed are as stable as

D. C. sols. D. C. sols also give a positive test for ionic gold; oscillatory current sols fail to so test[26].

The theory for the composition of the colloid here presented is essentially an outgrowth and continuation of that proposed by Beans in conjunction with Eastlack, Amsden, Low and Layton. It is believed that small gold particles are formed from the condensation of gold vapor produced by the arc and condensed by contact with the solution in which the sol is formed. Firmly bound to these particles are chloride ions held by the unsaturated electrical fields of force emanating from the gold atoms on the surface of the particles. Measurements and calculations indicate that the surface layer composition of these particles roughly corresponds to $AuCl^-$. The system represented in simplest form is:

$$[(Au_{46})\ Au.\ Cl^-\ x\ H_2O] + K^+ \,\|\, K^+ + Cl^-$$

These particles are held in solution by the chloride ions which homologate the surface of the complexes to the water by hydration. The amount of hydration and the corresponding stability depend on two factors: (1) the hydration of the chloride ions and (2) the difference in potential between the micellar group and the solution external thereto.

For sols formed by A. C. in 0.001 M KCl, using about 16-40 ohms in series with a 110 volt arc and with or without 1 m. f. in parallel with the arc, it is indicated that the radius of the average particle is about 2.9×10^{-6} cm. This particle carries about 10^5 chloride ions and about 47 times this number of gold atoms. The potential existing between its effective sphere of action and the solution which bathes it is indicated to be of the order of 150 m. v. This particle is believed to be, as expressed by McBain, an aggregate which resembles a large ion, carrying a large charge.

With the facts as stated above, this picture of the colloid is substantially in agreement. It is believed to be more comprehensive and inclusive than that proposed by Pauli. Pauli's theory of formation fails to account for colloid formation by Layton's method, Svedberg's method of blowing vapors into the solution, or the method of dispersing the gold in conductivity water and thereafter stirring in electrolyte, as well as for A. C. sol formation, since in none of these cases is measurable chlorine formed. In brief, Pauli's theory of formation will only account for those sols formed with D. C. since according to Pauli, electrolysis first forms chlorine which then converts the gold to gold chloride and thereafter $AuCl_4^-$ is formed. It might be pointed out that it is difficult to see why these $AuCl_4^-$ ions remain attached to the gold since gold chloride is exceedingly soluble in water. Moreover, it is experimentally indicated that the chlorine formed by electrolysis with D. C. is not sufficient to account for the chloride ion disappearing with the colloid formation.

As to the Werner complex, it has here been shown that boiling does not affect the conductivity of these sols. In this regard the gold sols here investigated are very different from Pennycuick's platinum sols, Bjerrum's chromium sols and the aluminum sols investigated by Whitehead[79]. Rugar has shown that these gold sols exhibit a maximum stability; too little as well as too much electrolyte causes instability, if the anion of the electrolyte forms gold compounds. But electrolyte having an anion which does not form gold compounds renders the colloid less stable in all concentrations. Scherer and Bjornstahl[80] have shown that colloidal gold gives the same X ray diffraction pattern as gold wire. With these facts the theory of complex gold Werner compounds does not seem to be in agreement. Sight should not be lost of the fact that substantially the only justification for Werner compounds lies in the presence of gold ions in D. C. sols.

The theory advanced here will on the other hand, satisfactorily account for the formation of the colloid by all methods cited, gives values for the size of the particle which are in good agreement with those measured by the ultramicroscope or ultracentrifuge, throws considerable light on why the concentration of electrolyte cannot exceed 0.02-0.05 moles per liter without having precipitation, and also offers a reasonable explanation of why the results which are obtained in measuring the same sol with a silver chloride concentration cell give an apparently greater value for the chloride ion removed than do conductimetric measurements.

Summary.

1. An improved method of arcing has been devised which substantially eliminates contamination, is semi-automatic, and possesses considerably more flexibility than methods previously employed.

2. It has been shown experimentally that Bredig colloids of gold may be prepared in aqueous potassium chloride solutions which are free from external contamination and undergo no appreciable electrolysis.

3. It has been shown that the heavy gold sediment, commonly called sludge, adsorbs no appreciable electrolyte, and thereby a source of error has been evaluated.

4. Centrifuging has no measurable effect on the conductivity of gold sols.

5. The gold electrolyte ratio in Bredig sols made in potassium chloride aqueous solutions has been evaluated by a new and more precise method of measurement.

6. It has been shown that Bredig gold sols made in aqueous potassium chloride solutions reach an approximate steady state in periods of about seven to ten days.

7. A particular study has been made of sols of low gold content, and it has been shown that such sols reach a steady state more rapidly than those of higher gold content.

8. Varied electrical circuits give sols having substantially the same ratio of gold to chloride provided an arc of approximately uniform size is maintained.

9. Bredig gold sols in aqueous potassium chloride solutions are practically unaffected by boiling under a reflux for periods up to one hour.

10. When Bredig gold sols are frozen, they release a portion of the electrolyte which is bound to the gold in stable sols, but the conductivity of the electrolyte solution never returns to the value obtained before sol formation.

11. Conductivity titrations are applicable to Bredig gold sols of low gold content and give virtually the same results as measurements by conductivity. Results resembling those of Beaver who measured sols made by D. C. are obtainable with sols made by A. C.

12. A new cell for measuring the changes in the chloride ion activity accompanying the formation of Bredig sols in aqueous potassium chloride solutions has been designed, and measurements which are more precise than those previously reported have been made therein.

13. It has been shown that the values obtained by comparable calculations of the size of particle in Bredig gold sols made by A. C. and the chloride ion content determined by conductivity, and those for sols made by Layton's method are approximately the same.

14. A theory is offered in explanation of the differences observed between determinations of chloride ion in Bredig gold sols by conductimetric and potentiometric measurements.

15. New calculations of the potential between the colloid and its environment are offered.

16. The observations of Beans and Eastlack on the nature of Bredig sols made in aqueous solutions have been extended, and additional evidence is offered demonstrating the fundamental correctness of the postulate advanced by these investigators to account for the nature of this Bredig colloid.

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Vita.

James Heyward Young was born in Cartersville, Georgia, April 27, 1899. He was Second Lieutenant of Infantry in the U. S. Army in 1918. He received the degree of Bachelor of Science from the University of Georgia in 1920. He was instructor in Chemistry at the University of Georgia in 1920-1921 and Adjunct Professor from 1921 to 1924.

He was a graduate student under the Faculty of Pure Science, Columbia University from February, 1925 to June, 1929. He served as Assistant in Inorganic, Organic, Qualitative, Quantitative and Physical Chemistry in Columbia University and Columbia University Extension, and as Lecturer in Quantitative Analysis in extension. He has been employed as chemist by the Roessler and Hasslacher Chemical Corporation since July, 1929.